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*With international search report.*(54) Title: **LUBRICANTS FOR HEAT TRANSFER FLUIDS**

## (57) Abstract

A heat transfer composition comprising a heat transfer medium and a lubricant, wherein said heat transfer medium is a low boiling organic compound and wherein said lubricant is a halogenated polyoxyalkylene monoalcohol having the empirical structural formula:  $R_1X_m(OR_2)_n-OH$  wherein  $R_1$  and  $R_2$  are independently selected from the group consisting of a straight or branched-chain alkyl group having 1 to 18 carbon atoms, an aryl group having from 6 to 18 carbon atoms, and combinations thereof,  $X$  is a halogen,  $m$  is an integer of between 1 and 37, and  $n$  is an integer from 5-350. Also claimed is the process for making the lubricant and the lubricant composition itself.

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LUBRICANTS FOR HEAT TRANSFER FLUIDS

The use of lubricants in heat transfer devices of the mechanical vapor recompression type, including  
5 refrigerators, heat pumps and air conditioning systems, is well known. In such devices, a working fluid of suitable boiling point evaporates at low pressure taking heat from the surrounding zone. The resulting vapor is then compressed and passed to a condenser where it  
10 condenses and gives off heat to a second zone. The condensate is then returned through an expansion valve to the evaporator, so completing the cycle. The mechanical energy required for compressing the vapor and pumping the fluid is provided by, for example, an  
15 electric motor or an internal combustion engine. As is the case with other mechanical equipment, it is necessary for the moving parts of the heat transfer devices to be adequately lubricated and the devices are generally designed to use lubricants which are miscible  
20 with the working fluids.

In the past, the heat transfer fluids typically used in these heat transfer devices were chlorofluorocarbons, such as dichlorodifluoromethane, together with a lubricant such as mineral oil. Today,  
25 the production of several of these chlorofluorocarbons is being severely limited by international agreement in order to protect the stratospheric ozone layer.

Unfortunately, some of the compounds, such as, for example, 1,1,1,2-tetrafluoroethane, which are being  
30 proposed as working fluids to replace dichlorodifluoromethane, are insufficiently miscible with mineral oils to allow the latter to be used as lubricants with these working fluids. Polyalkylene glycols have been proposed

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as alternative lubricants, but they are not entirely satisfactory for a number of reasons. For example, while polyalkylene glycols exhibit desired reverse solubility above a certain temperature such that the

5 working fluid tends to separate from the lubricant, for example at temperatures above about 40°C, they often attract water in an amount sufficient to cause corrosion in the equipment. More specifically, monols which rely upon ethylene oxide content to achieve sufficient

10 miscibility and viscosity to permit their use as lubricants, such as is disclosed in European Patent application 336,171 assigned to Nippon Oil Co., Ltd., and polypropylene glycol diols and triols such as is disclosed in U.S. Patent 4,755,316 assigned to

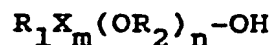
15 Allied-Signal Inc. all tend to attract more water than might be desired. Furthermore, these compounds often fail to wet metals sufficiently to provide efficient lubrication and have an adverse effect on aluminium commonly used for the construction of compressors.

20 The discovery of new lubricants for hydrofluorcarbon working fluids that do not suffer from the water affinity problems and the lack of wetting efficacy associated with known polyalkylene glycols, when utilized in a fluorocarbon working fluid, would be

25 highly desired by the heat transfer fluids community. Heretofore, an entirely satisfactory solution to those problems has not been proposed to the knowledge of the present inventors.

In one aspect, the present invention relates to a

30 halogenated polyoxyalkylene monoalcohol compound having the empirical structural formula:



wherein  $R_1$  and  $R_2$  are independently selected from the group consisting of a straight or

35 branched-chain alkyl group having 1 to 18 carbon atoms,

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an aryl group having from 6 to 18 carbon atoms, and combinations thereof, X is a halogen, m is an integer of between 1 and 37, and n is an integer from 5-350, preferably from about 10-50.

5 In another aspect, the present invention relates to a heat transfer composition comprising a heat transfer medium and a lubricant, wherein said heat transfer medium is a low boiling organic compound and wherein said lubricant is a halogenated polyoxyalkylene  
10 monoalcohol having the above identified empirical structural formula. The lubricant preferably has a molecular weight of at least about 500 and a viscosity of between about 20 cst. and about 320 cst.

In yet another aspect, the present invention  
15 relates to a process for producing a halogenated polyoxyalkylene monoalcohol having a molecular weight of between about 500 and about 20,000 by a reaction comprising:

(a) alkoxyating a halogenated monoalcohol in the  
20 presence of an acid or base catalyst to produce an alkoxyated halogenated monoalcohol having a molecular weight of between about 200 and about 500, and

(b) reacting said alkoxyated halogenated monoalcohol with an alkylene oxide in the presence of a  
25 double metal cyanide catalyst to produce a halogenated polyoxyalkylene monoalcohol having a molecular weight of between about 500 and about 20,000.

In accordance with the present invention, it has now been surprisingly found that a halogenated  
30 polyoxyalkylene monoalcohol having a molecular weight of at least about 500 (preferably at least about 600) is produced utilizing the two-step process of the present invention. This result is particularly unexpected since prior attempts to make these monoalcohols using  
35 conventional acid or base propoxylation catalysts provided a loss of catalyst activity after the addition

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of 7-10 moles of propylene oxide. Subsequent catalyst additions did not provide the desired higher molecular weight monoalcohol product. In contrast, the use of the double metal cyanide complex ("DMC") catalyst to  
5 increase the molecular weight of the monoalcohol after the initial propoxylation of trifluoroethanol with an acid or base catalyst provides a product having advantageous molecular weight and viscosity properties. The resulting halogenated polyoxyalkylene monoalcohol  
10 provides excellent utility as a lubricant for heat transfer media, particularly chlorofluorocarbon or hydrochlorofluorocarbon heat transfer media.

It has also been surprisingly found in accordance with the process of the present invention that the use  
15 of acid catalyst(s) in the production of propoxylated precursors for polyols makes it possible to produce the desired high molecular weight halogenated polyoxyalkylene monoalcohols directly in a DMC-catalyzed reaction without purification of the propoxylated  
20 precursors. Thus, the acid catalysts provide the desired catalysis for producing propoxylated precursors without deactivating or otherwise adversely affecting the DMC catalyst. Therefore, steps (a) and (b) of the process of the present invention can be conducted  
25 simultaneously or sequentially without catalyst residue removal prior to carrying out step (b) of the process. This result will be of significant value to lubricant manufacturers since it avoids the need to purify the propoxylated precursors prior to contacting with the DMC  
30 catalyst which is typically required if a base catalyst is utilized in step (a) of the process of the present invention.

The acid catalyst(s) useful in the process of the present invention are preferably Lewis acids, such as  
35  $\text{BF}_3\text{Et}_2\text{O}$  (boron trifluoride etherate),  $\text{SbF}_5$   
(antimony pentafluoride),  $\text{SbCl}_5$  (antimony

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pentachloride),  $F_3CSO_3H$  (trifluoromethane sulfonic acid), as well as protic acids such as  $HF_4$  (tetrafluoroboric acid),  $H_2SO_4$  (sulfuric acid), and combinations thereof, and the like.

5       The acid catalyst used in step (a) of the process of the present invention is typically employed in an amount of between about 0.01% and about two weight percent based upon the weight of the alkoxyated precursor-forming reaction mixture, preferably between  
10       about 50 and about 1,500 ppm in the reaction mixture. Exceeding the two percent upper limit of catalyst may result in undesirable side reactions.

      The base catalyst(s) useful in the process of the present invention is preferably selected from the group  
15       consisting of alkali metal hydroxides and alkaline earth metal hydroxides, alkali metal alkoxides, and combinations thereof. Typical base catalysts include potassium hydroxide, sodium hydroxide, magnesium hydroxide, calcium hydroxide, sodium methoxide,  
20       potassium methoxide, sodium ethoxide, potassium ethoxide, and combinations thereof. The base catalyst is typically employed in an amount of between about 0.1% and about four percent by weight based upon the weight of the alkoxyated precursor-forming reaction mixture.

25       The alkylene oxide utilized in steps (a) and (b) of the process of the present invention is preferably propylene oxide, although other alkylene oxides such as ethylene oxide, butylene oxide, amylene oxide, hexylene oxide, and aralkylene oxides such as styrene oxide, and  
30       the like, are within the scope of the present invention. Random or block addition of the oxyalkylene groups is suitably made in accordance with the process of the present invention. In the preparation of lubricants, oxyalkylene groups of 3 or more carbons are  
35       preferred since shorter chain groups tend to attract water to an extent sufficient to cause corrosion in the heat transfer equipment.

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In the preparation of lubricants, it is preferred that the halogenated polyoxyalkylene monoalcohol have a pour point of up to  $-10^{\circ}\text{C}$ , preferably  $-20$  to  $-50^{\circ}\text{C}$ . In a case where the pour point exceeds  $-10^{\circ}\text{C}$ , a

5 refrigerator oil composition containing such a high pour point lubricant is undesirably likely to solidify within the refrigeration system. In the preparation of lubricants, the number average molecular weight of the halogenated polyoxyalkylene monoalcohol preferably is  
10 between about 600 and about 3000 to provide enhanced compressor sealability.

The lubricant of the present invention is typically utilized in conjunction with a heat transfer fluid which is a low boiling organic compound(s). Illustrative heat  
15 transfer fluids include acetone, methanol, hydrocarbons such as butane and isobutane, halocarbons such as chlorofluorocarbons ("CFCs"), hydrochlorofluorocarbons ("HCFCs"), dichloromethane, hydrofluorocarbons, combinations thereof, and the like.

20 In the formula for the halogenated polyoxyalkylene monoalcohol,  $R_1$  is, for example, typically selected from the group of methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl  
25 or octadecyl, or benzyl or substituted benzyl. The preferred moiety is selected from methyl ethyl, propyl, butyl, pentyl, hexyl, octyl, decyl, octadecyl, and benzyl. X is a halogen selected from the group consisting of fluorine, chlorine, bromine and iodine ,  
30 and combinations thereof. Fluorine and chlorine are the most preferred halogens, and these are most advantageously utilized in the monoalcohol of the present invention as trifluoromethyl or trichloromethyl moieties.  $R_2$  is preferably selected from the group  
35 consisting of ethylene, propylene, trimethylene, butylene, 1,2-dimethylethylene, 1-methyltriethylene,



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2-methyltriethylene, tetramethylene and styrene, and combinations thereof. Of these, propylene, butylene and styrene are more preferred.

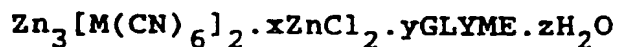
In the preparation of lubricants, it is also preferred that the kinematic viscosity of lubricant fall within the range of 15 to 500 cst at 100°F. In a case where the kinematic viscosity at 100°F is less than 15 cst a refrigeration oil will not maintain a sufficient degree of sealability. In a case where the refrigeration oil composition is intended to be used in low temperature recompression devices, the halogenated polyoxyalkylene monoalcohol preferably has a kinematic viscosity of between 20 and 420 cst, more preferably 26 to 220 cst at 100°F. In addition, the halogenated polyoxyalkylene monoalcohol of this invention preferably has a weight average molecular weight of 600 to 3000 to improve the compressor sealability.

The halogenated monoalcohol useful in the present invention is preferably trifluoroethanol, although other illustrative halogenated monoalcohols such as trichloroethanol, trifluoropropanol, dibromomonofluoroethanol, combinations thereof, and the like are within the scope of the present invention.

The double metal cyanide complex catalysts suitable for use in step (b) of the process of the present invention and their preparation are described in U.S. Pat. Nos. 4,472,560 and 4,477,589 to Shell Chemical Company and U.S. Pat. Nos. 3,941,849 and 4,335,188 to General Tire & Rubber Company. The DMC catalyst used in step (b) of the process of the present invention is typically employed in an amount of between about 0.01% and about four weight percent based upon the weight of the step (b) reaction mixture.

One double metal cyanide complex catalyst found particularly suitable for use is a zinc hexacyanometallate of formula:

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wherein M may be Co(III), or Cr(III) or Fe(II) or Fe(III); x, y, and z may be fractional numbers, integers, or zero and vary depending on the exact method  
5 of preparation of the complex, preferably independently being between 0 and 15.

The process of the present invention is suitably conducted at a temperature of between about 20°C and about 150°C, preferably between about 30°C and about  
10 120°C, although higher or lower temperatures may be used if desired. The reactions are suitably carried out at atmospheric pressure, although super- or sub-atmospheric pressures may be employed. The reaction times may vary from a few minutes to several hours or  
15 more depending upon the other reaction parameters.

The following examples are intended to illustrate, but in no way limit the scope of, the present invention.

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EXAMPLE 1Part A -Preparation of a Propoxylated Trifluoroethanol  
Precursor Using KOH Catalyst

A precursor was prepared by reacting propylene  
5 oxide (PO) with trifluoroethanol using potassium  
hydroxide (KOH) as catalyst. When the reaction ceased,  
more KOH and PO were added until the reaction stopped.  
The reaction mixture was then treated using conventional  
10 treatment for removal of KOH. This treated product had  
a viscosity of 26.7 centistokes (cst) at 100°F and a  
molecular weight of 600 as calculated from the hydroxyl  
number. Attempts to produce a higher molecular weight  
product using the KOH catalyst failed.

15 Part B -Preparation of a Propoxylated Trifluoroethanol  
Lubricant Using a Double Metal Cyanide Complex  
Catalyst

Fifteen pounds (6.8 kg) of the precursor prepared  
in Part A was charged to a 10-gallon (36 liter)  
stainless steel reactor in 1/3 increments. The zinc  
20 hexacyanocobaltate glyme complex (DMC) catalyst, 0.015  
pounds (6.8 grams) was dispersed into one of these  
additions of precursor. The reactor was sealed and  
purged with nitrogen.

The reactor was heated to  $230 \pm 10^\circ\text{F}$  ( $110 \pm 6^\circ\text{C}$ )  
25 and 2.7 pounds (1.2 kg) of PO added. After an  
initiation period of about 1.5 to 2 hours, the reaction  
began as evidenced by a decrease in pressure and an  
increase in temperature. An additional 14.2 pounds (6.4  
kg) of PO was added in a 2-hour period and post reacted  
30 to constant pressure in less than 1.5 hours. The  
viscosity at this point was 90 cst at 100°F, and the  
molecular weight was 1160.

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Even though the reaction mixture was cooled to about 100°F (38°C) and held overnight, the catalyst was still active the next day. An additional 5 pounds (2.3 kg) of PO was added at 230°F (110°C) in 70 minutes.

- 5 Removal of catalyst residues was then effected. A typical catalyst removal procedure is as follows: the mixture is post-reacted for thirty minutes, and then KOH (0.055 pounds, 0.025 kg.) and a filter aid such as diatomaceous earth (0.185 pounds, 0.084 kg.) is added,  
10 and the resulting mixture is stirred at 110°C for one hour, then vacuum stripped and filtered to provide a purified final product.

- The final product had a viscosity of 109 cst at 100.0°F (37.7°C) and a hydroxyl number of 42.5. The  
15 calculated molecular weight for the product is 1320.

#### Part C - Testing of the Product as a Lubricant

- Miscibility Test - A miscibility determination was made by visually observing if the lubricant was clear to slightly hazy (and thus was designated "miscible") or  
20 was cloudy or phase separated (and thus was designated "immiscible") in R-134a (1,2,2,2-tetrafluoroethane) fluid. The product produced in Part B above was found to be miscible in R-134a at a concentration level of 10%, 20%, and 30% by weight. In contrast, a comparison  
25 formulation of polyoxylated n-butanol having a slighter lower molecular weight of 1000 and containing no halogen was found to be immiscible in R-134a at a concentration level of 10% and a temperature of 120°F. Such immiscibility is unacceptable for a lubricant for R-134a.  
30 As another comparison, another halogen-free monoalcohol, namely polyoxypropylene monobutylalcohol, having a higher molecular weight of 1850 was found to also be immiscible in R-134a at a concentration level of 20% and a temperature of 120°F. Such immiscibility is  
35 unacceptable for a lubricant for R-134a.

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Although the propoxylated trifluoroethanol precursor produced in Part A above was found to be miscible in R-134a at a concentration level of 20%, this precursor had an undesirably low viscosity of 20 cst

5 which is too low to function as an effective lubricant.

Four-Ball Test - ASTM-D-2783 - This test was conducted in accordance with the ASTM procedure in order to measure the "Load Wear Index" or LWI as an indicator of the lubricating efficacy of the product produced in

10 Part B above. Briefly, this ASTM procedure is conducted with one steel ball under load rotating against three steel balls held stationary in the form of a cradle. Test lubricant covers the lower three balls, and the rotating speed is 1760 rpm plus or minus 40 rpm. The

15 testing apparatus and test lubricant are brought up to a temperature of 18-35°C and then a series of duration tests are conducted until welding occurs.

Following this testing regimen, the product produced in Part B above was found to have an LWI of

20 25.5. In contrast, a comparison formulation was tested employing a halogen-free polyoxypropylene monobutylalcohol lubricant, having a lower molecular weight of 750 and viscosity of 35 cst at 100°F, and this comparison formulation provided an LWI of only 20.9.

25

## EXAMPLE 2

### Part A -Preparation of a Propoxylated Trifluoroethanol Precursor Using Antimony Pentafluoride as a Catalyst

2,2,2-trifluoroethanol (50 grams, 0.50 equivalent) was added to a flask under nitrogen, and antimony

30 pentafluoride (0.05 grams, 0.23 miliequivalent) was added to the flask. Propylene oxide (200 grams, 3.44 equivalents) was added dropwise over a period of one hour. After stirring for an additional 15 minutes, the

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temperature was raised to 65°C and the fact that no PO refluxed indicated that the reaction was complete. The product had a hydroxyl number of 112.

In a similar manner propoxylated trifluoroethanol precursors were prepared with  $\text{BF}_3$  and  $\text{SbCl}_5$  catalysts.

Part B - Preparation of a Propoxylated Trifluoroethanol Lubricant with Double Metal Cyanide Catalyst and a Precursor Prepared with  $\text{SbF}_5$

10 A portion of the precursor prepared with  $\text{SbF}_5$  catalyst described in Part A (100g, 0.20 eq.) was added to a one liter autoclave without removal of the antimony pentafluoride and zinc hexacyanocobaltate glyme catalyst (0.64g) was added and the mixture was heated to 100C.

15 Propylene oxide (30g, 0.52 eq.) was added and after 20 minutes a pressure drop indicated that the catalyst was activated. An additional 428 grams of PO (7.4 eq.) was added over a 90 minute period and the pressure remained below 30 psi indicating that the PO was reacting

20 rapidly. When the pressure fell below 10 psi, powdered KOH (2.5g, 0.045 eq.) was added, and the mixture was heated at 110°C for 1 hour. Magnesium silicate was added and the mixture was stirred at 110°C for another hour then vacuum stripped for 2 hours and then

25 filtered. The product had a hydroxyl number of 20.1 and a calculated molecular weight of 2790 and was useful as a lubricant.

EXAMPLE 3

Preparation of a High Molecular Weight Propoxylated Trifluoroethanol Lubricant

30 A propoxylated trifluoroethanol precursor was prepared with  $\text{SbCl}_5$  as described in Example 2 and 100g

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(0.2 eq.) of this precursor was added to a one liter autoclave. Zinc hexacyanocobaltate glyme catalyst (0.64g) was added and the mixture was flushed three times with nitrogen and heated to 100°C. Propylene

5 oxide (30g, 0.52 eq.) was added and after 20 minutes a pressure drop indicated that the catalyst was activated. An additional 570g (9.81 eq.) of PO were added over a period of 90 minutes. When the pressure fell below 10 psi, 550g of the mixture was removed from

10 the reactor to allow for addition of more oxide. To the 150g remaining in the reactor (150g, 3704 eq. wt., 0.0405 eq.) was added an additional 175 grams of PO over a period of 1 hour. After a post reaction of 30 minutes, KOMe (1.6g) was added, and the mixture was

15 heated at 110°C for 1 hour. Magnesium silicate 4.9g was added and the mixture was heated at 110C for an additional hour and then vacuum stripped for 2 hours. The mixture was then filtered to yield a product with a hydroxyl number of 7.0 and a calculated molecular weight

20 of 8,000.

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WHAT IS CLAIMED IS:

1. A heat transfer composition comprising a heat transfer medium and a lubricant, characterized in that in said heat transfer medium is a low boiling organic compound and wherein said lubricant is a halogenated polyoxyalkylene monoalcohol having the empirical structural formula:



- wherein  $R_1$  is selected from the group consisting of a straight or branched-chain alkyl group having 1 to 18 carbon atoms, an aryl group having from 6 to 18 carbon atoms, and combinations thereof, wherein  $R_2$  is selected from the group consisting of a straight or branched-chain alkylene group having 1 to 18 carbon atoms, an arylene group having from 6 to 18 carbon atoms, and combinations thereof, X is a halogen, m is an integer of between 1 and 37, and n is an integer from 5-350.

2. The heat transfer composition of claim 1 characterized in that said heat transfer medium comprises a chlorofluorocarbon, a hydrofluorocarbon, a fluorocarobon, or a combination thereof.

3. The composition of claim 1 characterized in that n has a value of between 10 and 50.

4. The composition of claim 1 characterized in that said lubricant has a molecular weight of at least about 500 and a viscosity of between about 20 cst and about 320 cst.

5. A process for producing a halogenated polyoxyalkylene monoalcohol having a molecular weight of



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between about 500 and about 20,000 by a reaction characterized by:

- 5 (a) alkoxyating a halogenated monoalcohol in the presence of an acid or base catalyst to produce an alkoxyated halogenated monoalcohol having a molecular weight of between about 200 and about 500, and
- (b) reacting said alkoxyated halogenated
- 10 monoalcohol with an alkylene oxide in the presence of a double metal cyanide catalyst to produce a halogenated polyoxyalkylene monoalcohol having a molecular weight of between about 500 and about 20,000.

6. The process of claim 5 characterized in that the catalyst of step (a) is a base catalyst selected from the group consisting of alkali metal hydroxides, alkaline earth metal hydroxides, alkali metal alkoxides,

5 and combinations thereof, and wherein removal of base catalyst residues is effected prior to carrying out step (b).

7. The process of claim 5 characterized in that the catalyst of step (a) is an acid catalyst and wherein steps (a) and (b) are carried out simultaneously without removal of step (a) catalyst residues prior to carrying

5 out step (b).

8. The process of claim 5 characterized in that the catalyst of step (a) is an acid catalyst and wherein steps (a) and (b) are carried out sequentially without removal of step (a) catalyst residues prior to carrying

5 out step (b).

9. The process of claim 5 characterized in that the catalyst of step (a) is an acid catalyst selected from the group consisting of:  $\text{BF}_3\text{Et}_2\text{O}$  (boron trifluoride etherate),  $\text{SbF}_5$  (antimony pentafluoride),  $\text{SbCl}_5$

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5 (antimony pentachloride),  $F_3CSO_3H$  (trifluoromethane sulfonic acid),  $HB F_4$  (tetrafluoroboric acid),  $H_2SO_4$  (sulfuric acid), and combinations thereof.

10. The process of claim 5 characterized in that the catalyst of step (a) is an acid catalyst employed in an amount of between about 0.01% and about two weight percent based upon the weight of the step (a) reaction mixture.

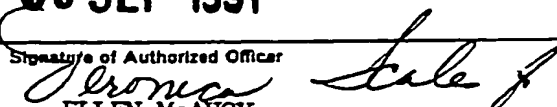
11. The process of claim 5 characterized in that the catalyst of step (a) is an acid catalyst employed in an amount of 50 and about 1,500 ppm in the step (a) reaction mixture.

12. The process of claim 5 characterized in that the catalyst of step (a) is a base catalyst employed in an amount of between about 0.1% and about four percent by weight based upon the weight of the step (a) reaction mixture.

13. The process of claim 5 characterized in that the double metal cyanide catalyst of step (b) is employed in an amount of between about 0.01% and about four weight percent based upon the weight of the step (b) reaction mixture.

# INTERNATIONAL SEARCH REPORT

International Application No. PCT/US91/03683

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) <sup>6</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC		
INT. CL(5) C09K 5/04		
U.S. CL. 252/68		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
US	252/52A, 54, 67, 68; 568/614, 615	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT <sup>9</sup></b>		
Category <sup>9</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
P, &	US, A, 5,002,678, (VANOVER ET AL) 26 MARCH 1991 SEE ENTIRE DOCUMENT	1-13
A P	US, A, 4,948,525, (SASAKI ET AL), 14 AUGUST 1990 SEE ENTIRE DOCUMENT	1-4
A	US, A, 4,755,316, (MAGID ET AL), 5 JULY 1988 SEE ENTIRE DOCUMENT	1-4
A	US, A, 3,829,508, (DIERY ET AL), 13 AUGUST 1974 SEE ABSTRACT	5-13
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A	EP, A, 200,403, (BRITISH PETROLEUM), 5 NOVEMBER 1986, SEE ABSTRACT	5-13
<div style="display: flex; justify-content: space-between;"> <div style="width: 48%;"> <p><sup>10</sup> Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 48%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&amp;" document member of the same patent family</p> </div> </div>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
SEPTEMBER 21, 1991	30 SEP 1991	
International Searching Authority	Signature of Authorized Officer	
ISA/US	 ELLEN MCAVOY	